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- (71) Applicant (for all designated States except US): **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US];  
1007 Market Street, Wilmington, DE 19898 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **SCHIFFINO, Rinaldo, S.** [US/US]; 4809 Threadneedle Road, Wilmington, DE 19807 (US).
- (74) Agent: **LERMAN, Bart, E.**; E.I. Dupont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).
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(54) Title: CONTINUOUS MANUFACTURING PROCESS FOR  $\alpha$ -OLEFINS

(57) Abstract: A manufacturing process for  $\alpha$ -olefins using certain iron containing ethylene oligomerization catalysts together with alkylaluminum cocatalysts, in which using a low ratio of Al:Fe in the process results in a lowered formation of undesired polyethylene waxes and polymer. This results in less fouling of the process lines and vessels in the manufacturing plant.

TITLECONTINUOUS MANUFACTURING PROCESS FOR  $\alpha$ -OLEFINSFIELD OF THE INVENTION

A continuous manufacturing process for  $\alpha$ -olefins using certain iron containing ethylene oligomerization catalysts together with alkylaluminum cocatalysts, in which using a low ratio of Al:Fe in the process results in a lowered formation of undesired polyethylene waxes and polymer.

TECHNICAL BACKGROUND

$\alpha$ -Olefins are important items of commerce, billions of kilograms being manufactured yearly. They are useful as monomers for (co)polymerizations and as chemical intermediates for the manufacture of many other materials, for example detergents and surfactants. Presently most  $\alpha$ -olefins are made by the catalyzed oligomerization of ethylene by various catalysts, especially certain nickel complexes or aluminum alkyls, see for instance US4020121 and I. Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4<sup>th</sup> Ed., Vol. 17, John Wiley & Sons, New York, p 839-858.

Recently, as reported in US5955555 and US6103946, both of which are hereby incorporated by reference herein for all purposes as if fully set forth, it has been found that iron complexes of certain tridentate ligands are excellent catalysts for the production of  $\alpha$ -olefins from ethylene. Among the options for using such catalysts are those in which the iron complexes are used in conjunction with a cocatalyst, particularly an alkylaluminum cocatalyst such as an alkylaluminumoxane.

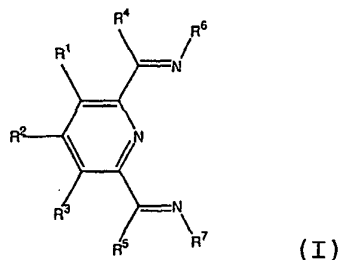
It has recently been found, particularly in continuous processes using such iron complexes, that high molar ratios of Al:Fe lead to the undesirable formation of polyethylene waxes and polymers, which tend to foul the oligomerization

apparatus. It has now been found that lower Al:Fe ratios diminish the formation of these undesirable polyethylenes, while not otherwise significantly deleteriously affecting the process.

#### SUMMARY OF THE INVENTION

This invention concerns a method for reducing the formation of polyethylene waxes and polymers in a continuous process for the production of a linear  $\alpha$ -olefin product, said continuous process comprising the step of contacting, in a continuous reactor, process ingredients comprising an ethylene oligomerization catalyst composition, ethylene and a cocatalyst, wherein:

(a) the ethylene oligomerization catalyst composition comprises an iron complex of a compound of the formula



wherein:

$R^1$ ,  $R^2$  and  $R^3$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of  $R^1$ ,  $R^2$  and  $R^3$  vicinal to one another taken together may form a ring;

$R^4$  and  $R^5$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

$R^6$  and  $R^7$  are each independently a substituted aryl having a first ring atom bound to the imino nitrogen, provided that:

in  $R^6$ , a second ring atom adjacent to said first ring atom is bound to a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and further provided that

in R<sup>6</sup>, when said second ring atom is bound to a halogen or a primary carbon group, none, one or two of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a halogen or a primary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a secondary carbon group, none, one or two of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a halogen, a primary carbon group or a secondary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a tertiary carbon group, none or one of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a tertiary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; and

(b) the cocatalyst comprises an alkyl aluminum compound;

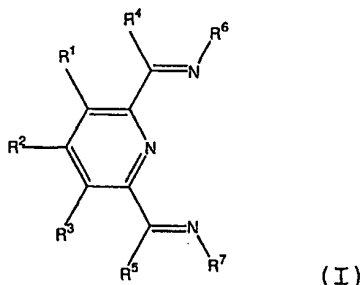
said method for reducing comprising the step of contacting said process ingredients in amounts such that the molar ratio of Al in the cocatalyst to Fe in the ethylene oligomerization catalyst is about 2000 or less.

Stated another way, the present invention concerns the use, in the aforementioned continuous process, of a molar ratio of Al in the cocatalyst to Fe in the ethylene oligomerization catalyst is about 2000 or less, to reduce the formation of polyethylene waxes and polymers in such a continuous process.

The present invention also concerns a continuous process for the production of a linear  $\alpha$ -olefin product, the process comprising the step of contacting, in a continuous reactor, process ingredients comprising an ethylene oli-

gomerization catalyst composition, ethylene and a cocatalyst, wherein:

(a) the ethylene oligomerization catalyst composition comprises an iron complex of a compound of the formula



wherein:

$R^1$ ,  $R^2$  and  $R^3$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of  $R^1$ ,  $R^2$  and  $R^3$  vicinal to one another taken together may form a ring;

$R^4$  and  $R^5$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

$R^6$  and  $R^7$  are each independently a substituted aryl having a first ring atom bound to the imino nitrogen, provided that:

in  $R^6$ , a second ring atom adjacent to said first ring atom is bound to a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and further provided that

in  $R^6$ , when said second ring atom is bound to a halogen or a primary carbon group, none, one or two of the other ring atoms in  $R^6$  and  $R^7$  adjacent to said first ring atom are bound to a halogen or a primary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in  $R^6$ , when said second ring atom is bound to a secondary carbon group, none, one or two of the other ring atoms in  $R^6$  and  $R^7$  adjacent to said first ring atom are bound to a

halogen, a primary carbon group or a secondary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a tertiary carbon group, none or one of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a tertiary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; and

(b) the cocatalyst comprises an alkyl aluminum compound;

characterized in that the molar ratio of Al in the cocatalyst to Fe in the ethylene oligomerization catalyst is from about 5 to about 300.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description. It is to be appreciated that certain features of the invention which are, for clarity, described below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein, certain terms are used. Some of them are:

A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. As examples of hydrocarbyls may be mentioned unsubstituted alkyls, cycloalkyls and aryls. If not otherwise stated, it is preferred that hydrocarbyl groups (and alkyl groups) herein contain 1 to about 30 carbon atoms.

By "substituted hydrocarbyl" herein is meant a hydrocarbyl group that contains one or more substituent groups

which are inert under the process conditions to which the compound containing these groups is subjected (e.g., an inert functional group, see below). The substituent groups also do not substantially detrimentally interfere with the oligomerization process or operation of the oligomerization catalyst system. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are rings containing one or more heteroatoms, such as nitrogen, oxygen and/or sulfur, and the free valence of the substituted hydrocarbyl may be to the heteroatom. In a substituted hydrocarbyl, all of the hydrogens may be substituted, as in trifluoromethyl.

By "(inert) functional group" herein is meant a group, other than hydrocarbyl or substituted hydrocarbyl, which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially deleteriously interfere with any process described herein that the compound in which they are present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), and ether such as  $-OR^{50}$  wherein  $R^{50}$  is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a transition metal (Fe) atom, the functional group alone should not coordinate to the metal atom (Fe) more strongly than the groups in those compounds that are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

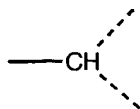
By a "cocatalyst" or a "catalyst activator" is meant one or more compounds that react with a transition metal compound to form an activated catalyst species. One such catalyst activator is an "alkyl aluminum compound" which, herein, is meant a compound in which at least one alkyl

group is bound to an aluminum atom. Other groups such as, for example, alkoxide, hydride and halogen may also be bound to aluminum atoms in the compound.

By a "linear  $\alpha$ -olefin product" is meant a composition predominantly comprising a compound (or mixture of compounds) of the formula  $H(CH_2CH_2)_qCH=CH_2$  wherein  $q$  is an integer of 1 to about 18. In most cases, the linear  $\alpha$ -olefin product of the present process will be a mixture of compounds having differing values of  $q$  of from 1 to 18, with a minor amount of compounds having  $q$  values of more than 18. Preferably less than 50 weight percent, and more preferably less than 20 weight percent, of the product will have  $q$  values over 18. The product may further contain small amounts (preferably less than 30 weight percent, more preferably less than 10 weight percent, and especially preferably less than 2 weight percent) of other types of compounds such as alkanes, branched alkenes, dienes and/or internal olefins.

By a "primary carbon group" herein is meant a group of the formula  $-CH_2---$ , wherein the free valence  $---$  is to any other atom, and the bond represented by the solid line is to a ring atom of a substituted aryl to which the primary carbon group is attached. Thus the free valence  $---$  may be bonded to a hydrogen atom, a halogen atom, a carbon atom, an oxygen atom, a sulfur atom, etc. In other words, the free valence  $---$  may be to hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group. Examples of primary carbon groups include  $-CH_3$ ,  $-CH_2CH(CH_3)_2$ ,  $-CH_2Cl$ ,  $-CH_2C_6H_5$ ,  $-OCH_3$  and  $-CH_2OCH_3$ .

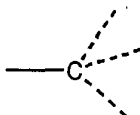
By a "secondary carbon group" is meant the group





wherein the bond represented by the solid line is to a ring atom of a substituted aryl to which the secondary carbon group is attached, and both free bonds represented by the dashed lines are to an atom or atoms other than hydrogen. These atoms or groups may be the same or different. In other words the free valences represented by the dashed lines may be hydrocarbyl, substituted hydrocarbyl or inert functional groups. Examples of secondary carbon groups include  $-\text{CH}(\text{CH}_3)_2$ ,  $-\text{CHCl}_2$ ,  $-\text{CH}(\text{C}_6\text{H}_5)_2$ , cyclohexyl,  $-\text{CH}(\text{CH}_3)\text{OCH}_3$ , and  $-\text{CH}=\text{CCH}_3$ .

By a "tertiary carbon group" is meant a group of the formula



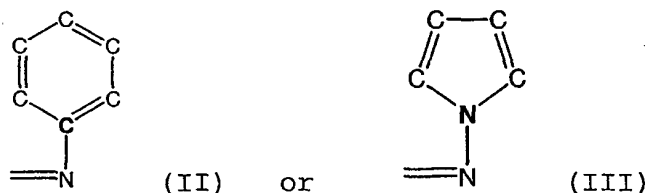
wherein the bond represented by the solid line is to a ring atom of a substituted aryl to which the tertiary carbon group is attached, and the three free bonds represented by the dashed lines are to an atom or atoms other than hydrogen. In other words, the bonds represented by the dashed lines are to hydrocarbyl, substituted hydrocarbyl or inert functional groups. Examples of tertiary carbon groups include  $-\text{C}(\text{CH}_3)_3$ ,  $-\text{C}(\text{C}_6\text{H}_5)_3$ ,  $-\text{CCl}_3$ ,  $-\text{CF}_3$ ,  $-\text{C}(\text{CH}_3)_2\text{OCH}_3$ ,  $-\text{C}\equiv\text{CH}$ ,  $-\text{C}(\text{CH}_3)_2\text{CH}=\text{CH}_2$ , aryl and substituted aryl such as phenyl and 1-adamantyl.

By "aryl" is meant a monovalent aromatic group in which the free valence is to the carbon atom of an aromatic ring. An aryl may have one or more aromatic rings which may be fused, connected by single bonds or other groups.

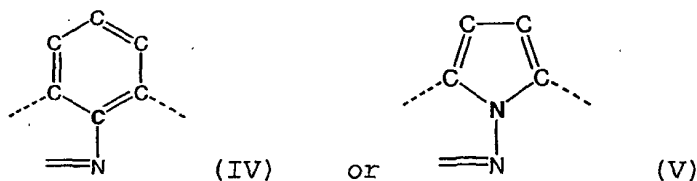
By "substituted aryl" is meant a monovalent aromatic group substituted as set forth in the above definition of "substituted hydrocarbyl". Similar to an aryl, a substituted aryl may have one or more aromatic rings which may be

fused, connected by single bonds or other groups; however, when the substituted aryl has a heteroaromatic ring, the free valence in the substituted aryl group can be to a heteroatom (such as nitrogen) of the heteroaromatic ring instead of a carbon.

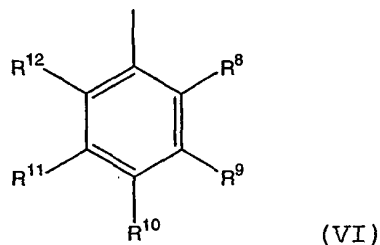
By a "first ring atom in  $R^6$  and  $R^7$  bound to an imino nitrogen atom" is meant the ring atom in these groups bound to an imino nitrogen shown in (I), for example



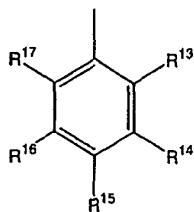
the atoms shown in the 1-position in the rings in (II) and (III) are the first ring atoms bound to an imino carbon atom (other groups which may be substituted on the aryl groups are not shown). Ring atoms adjacent to the first ring atoms are shown, for example, in (IV) and (V), where the open valencies to these adjacent atoms are shown by dashed lines (the 2,6-positions in (IV) and the 2,5-positions in (V)).



In one preferred compound (I)  $R^6$  is



and  $R^7$  is



(VII)

wherein:

$R^8$  is a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

provided that:

when  $R^8$  is a halogen or primary carbon group none, one or two of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  are a halogen or a primary carbon group, with the remainder of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  being hydrogen; or

when  $R^8$  is a secondary carbon group, none or one of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  is a halogen, a primary carbon group or a secondary carbon group, with the remainder of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  being hydrogen; or

when  $R^8$  is a tertiary carbon group, none or one of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  is tertiary carbon group, with the remainder of  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  being hydrogen;

and further provided that any two of  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  vicinal to one another, taken together may form a ring.

In the above formulas (VI) and (VII),  $R^8$  corresponds to the second ring atom adjacent to the first ring atom bound to the imino nitrogen, and  $R^{12}$ ,  $R^{13}$  and  $R^{17}$  correspond to the other ring atoms adjacent to the first ring atom.

In compounds (I) containing (VI) and (VII), it is particularly preferred that:

if  $R^8$  is a primary carbon group,  $R^{13}$  is a primary carbon group, and  $R^{12}$  and  $R^{17}$  are hydrogen; or

if  $R^8$  is a secondary carbon group,  $R^{13}$  is a primary carbon group or a secondary carbon group, more preferably a secondary carbon group, and  $R^{12}$  and  $R^{17}$  are hydrogen; or

if  $R^8$  is a tertiary carbon group (more preferably a trihalo tertiary carbon group such as a trihalomethyl),  $R^{13}$  is a tertiary carbon group (more preferably a trihalotertiary group such as a trihalomethyl), and  $R^{12}$  and  $R^{17}$  are hydrogen; or

if  $R^8$  is a halogen,  $R^{13}$  is a halogen, and  $R^{12}$  and  $R^{17}$  are hydrogen.

In all specific preferred compounds (I) in which (VI) and (VII) appear, it is preferred that  $R^1$ ,  $R^2$  and  $R^3$  are hydrogen; and/or  $R^4$  and  $R^5$  are methyl. It is further preferred that:

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is methyl; and  $R^8$  is a primary carbon group, more preferably methyl; or

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is ethyl; and  $R^8$  is a primary carbon group, more preferably ethyl; or

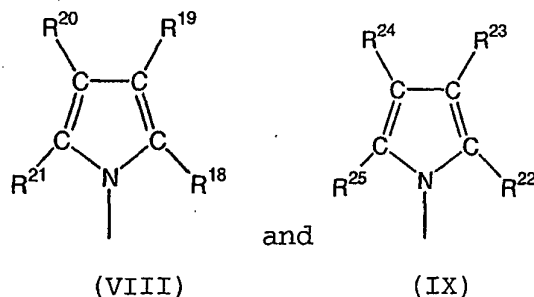
$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is isopropyl; and  $R^8$  is a primary carbon group, more preferably isopropyl; or

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is n-propyl; and  $R^8$  is a primary carbon group, more preferably n-propyl; or

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is chloro; and  $R^8$  is a halogen, more preferably chloro; or

$R^9$ ,  $R^{10}$ ,  $R^{11}$ ,  $R^{12}$ ,  $R^{14}$ ,  $R^{15}$ ,  $R^{16}$  and  $R^{17}$  are all hydrogen;  $R^{13}$  is trihalomethyl, more preferably trifluoromethyl; and  $R^8$  is a trihalomethyl, more preferably trifluoromethyl.

In another preferred embodiment of (I),  $R^6$  and  $R^7$  are, respectively



wherein:

$R^{18}$  is a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and

$R^{19}$ ,  $R^{20}$ ,  $R^{23}$  and  $R^{24}$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

Provided that:

when  $R^{18}$  is a halogen or primary carbon group none, one or two of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  are a halogen or a primary carbon group, with the remainder of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  being hydrogen; or

when  $R^{18}$  is a secondary carbon group, none or one of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  is a halogen, a primary carbon group or a secondary carbon group, with the remainder of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  being hydrogen;

when  $R^{18}$  is a tertiary carbon group, none or one of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  is a tertiary carbon group, with the remainder of  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  being hydrogen;

and further provided that any two of  $R^{18}$ ,  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{22}$ ,  $R^{23}$ ,  $R^{24}$  and  $R^{25}$  vicinal to one another, taken together may form a ring.

In the above formulas (VIII) and (IX),  $R^{18}$  corresponds to the second ring atom adjacent to the first ring atom

bound to the imino nitrogen, and  $R^{21}$ ,  $R^{22}$  and  $R^{25}$  correspond to the other ring atoms adjacent to the first ring atom.

In compounds (I) containing (VIII) and (IX), it is particularly preferred that:

if  $R^{18}$  is a primary carbon group,  $R^{22}$  is a primary carbon group, and  $R^{21}$  and  $R^{25}$  are hydrogen; or

if  $R^{18}$  is a secondary carbon group,  $R^{22}$  is a primary carbon group or a secondary carbon group, more preferably a secondary carbon group, and  $R^{21}$  and  $R^{25}$  are hydrogen; or

if  $R^{18}$  is a tertiary carbon group (more preferably a trihalo tertiary carbon group such as a trihalomethyl),  $R^{22}$  is a tertiary carbon group (more preferably a trihalotertiary group such as a trihalomethyl), and  $R^{21}$  and  $R^{25}$  are hydrogen; or

if  $R^{18}$  is a halogen,  $R^{22}$  is a halogen, and  $R^{21}$  and  $R^{25}$  are hydrogen.

In all specific preferred compounds (I) in which (VIII) and (IX) appear, it is preferred that  $R^1$ ,  $R^2$  and  $R^3$  are hydrogen; and/or  $R^4$  and  $R^5$  are methyl. It is further preferred that:

$R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{23}$  and  $R^{24}$  are all hydrogen;  $R^{22}$  is methyl; and  $R^{18}$  is a primary carbon group, more preferably methyl; or

$R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{23}$  and  $R^{24}$  are all hydrogen;  $R^{22}$  is ethyl; and  $R^{18}$  is a primary carbon group, more preferably ethyl; or

$R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{23}$  and  $R^{24}$  are all hydrogen;  $R^{22}$  is isopropyl; and  $R^{18}$  is a primary carbon group, more preferably isopropyl; or

$R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{23}$  and  $R^{24}$  are all hydrogen;  $R^{22}$  is n-propyl; and  $R^{18}$  is a primary carbon group, more preferably n-propyl; or

$R^{19}$ ,  $R^{20}$ ,  $R^{21}$ ,  $R^{23}$  and  $R^{24}$  are all hydrogen;  $R^{22}$  is chloro or bromo; and  $R^{18}$  is a halogen, more preferably chloro or bromo.

Compound (I) and its iron complexes (the oligomerization catalyst) may be prepared by a variety of methods, see for instance previously incorporated US5955555 and US6103946, as well as US6232259 and WO00/08034, both of which are also incorporated by reference herein for all purposes as if fully set forth.

It is preferred herein to react an iron complex of (I), such as a complex of (I) with  $\text{FeCl}_2$ , with the cocatalyst (e.g., the alkylaluminum compound), preferably an aluminoxane such as methylaluminoxane, to form an active ethylene oligomerization species. The molar ratio of aluminum (as alkylaluminum compound) to iron (as a complex) in the oligomerization preferably is about 2000 or less. A more preferred upper limit is about 1500 or less, still more preferably about 1000 or less, and especially about 700 or less; and as a lower limit is about 5 or more, more preferably about 10 or more, still more preferably about 100 or more, even more preferably about 300 or more, and especially about 500 or more. For clarity, any combination of the aforementioned upper and lower limits may be used to define a preferred range herein such as, for example, from about 5 to about 1500, from about 5 to about 1000, from about 100 to about 1000, from about 500 to about 700, and other other such combination.

Another preferred range in accordance with the present invention is from about 5 to about 300. Within this range, a more preferred lower limit is about 10 or more, more preferably about 20 or more, still more preferably about 30 or more, and especially about 50 or more; and a more preferred upper limit about 200 or less, still more preferably about 150 or less, and especially about 100 or less. Again for clarity, any combination of the aforementioned upper and lower limits may be used to define a preferred range herein.

It should be noted that the above ranges refer to steady state operating conditions. Under certain circumstances, it may be beneficial to start the reaction under higher Al:Fe ratios then, in the course of the process stabilizing, lower the Al:Fe ratio to the desired steady state level. For example, the reaction could be started at above any of the upper ratio limits mentioned above, then reduced to the desired level at or above any of the lower ratio limits mentioned above.

Preferred alkylaluminum compounds include one or more of  $R^{51}_3Al$ ,  $R^{51}AlCl_2$ ,  $R^{51}_2AlCl$ , and " $R^{51}AlO$ " (alkylaluminumoxanes), wherein  $R^{51}$  is alkyl containing 1 to 25 carbon atoms, preferably 1 to 4 carbon atoms. Specific alkylaluminum compounds include methylaluminumoxane (which is an oligomer with the general formula  $(MeAlO)_n$ ),  $(C_2H_5)_2AlCl$ ,  $C_2H_5AlCl_2$ ,  $(C_2H_5)_3Al$  and  $((CH_3)_2CHCH_2)_3Al$ . A preferred alkylaluminum compound is an aluminumoxane, especially methyl aluminumoxane.

The conditions for the oligomerization described in previously incorporated US6103946 and United States Appl. Ser. No. 09/906,974 (filed July 17, 2001), entitled "MANUFACTURING PROCESS FOR ALPHA-OLEFINS" (corresponding to PCT Appln. PCT/US01/22628, filed July 18, 2001), may otherwise be followed.

For example, the oligomerization reaction may be run at a wide range of temperatures generally ranging from about  $-100^\circ C$  to about  $+300^\circ C$ , preferably about  $0^\circ C$  to about  $200^\circ C$ , and more preferably about  $20^\circ C$  to about  $100^\circ C$ . Pressures may also vary widely, ranging from an ethylene pressure (gauge) of from about 0 kPa to about 35 MPa, more preferably from about 500 kPa to about 15 MPa.

The process may be run in gas or liquid phase, but is typically run in liquid phase, preferably using an aprotic organic liquid. The process ingredients and products may or



may not be soluble in these liquids, but obviously these liquids should not prevent the oligomerization from occurring. Suitable liquids include alkanes, alkenes, cycloalkanes, selected halogenated hydrocarbons and aromatic hydrocarbons. Specific useful liquids include hexane, toluene, benzene and the  $\alpha$ -olefins themselves.

The ethylene oligomerizations herein may also initially be carried out in the solid state by, for instance, supporting and active catalyst and/or aluminum compound on a substrate such as silica or alumina. Alternatively a solution of the catalyst precursor may be exposed to a support having an alkylaluminum compound on its surface. These "heterogeneous" catalysts may be used to catalyze oligomerization in the gas phase or the liquid phase. By "gas phase" is meant that the ethylene is transported to contact with the catalyst particle while the ethylene is in the gas phase. In general, the oligomerization may be run as a continuous gas phase, solution or slurry processes.

It is particularly preferred to run the oligomerization as "essentially single phase liquid full", which means that at least 95 volume percent of the reactor volume is occupied by a liquid that is a single phase. Small amounts of the reactor volume may be taken up by gas, for example ethylene may be added to the reactor as a gas, which dissolves rapidly under the process conditions. Nevertheless, some small amount of dissolving ethylene gas may be present. Not counted in the reactor volume is any solid resulting from fouling of the reactor. See, for example, previously incorporated United States Appl. Ser. No. 09/ Ser. No. 09/906,974 (filed July 17, 2001), entitled "MANUFACTURING PROCESS FOR ALPHA-OLEFINS" (corresponding to PCT Appln. PCT/US01/22628, filed July 18, 2001).

These molar ratios of Al:Fe described herein are based on the process ingredients, that is, the ingredients comprising the reactor feed; therefore, it is preferred at such low molar Al:Fe ratios to purify the process ingredients so that the alkylaluminum compounds are not "used up" reacting with moisture or other impurities.

Using the oligomerization catalysts described herein a mixture of  $\alpha$ -olefins is obtained. A measure of the molecular weights of the olefins obtained is factor K from the Schulz-Flory theory (see for instance B. Elvers, et al., Ed. Ullmann's Encyclopedia of Industrial Chemistry, Vol. A13, VCH Verlagsgesellschaft mbH, Weinheim, 1989, p. 243-247 and 275-276). This is defined as:

$$K = n(C_{n+2} \text{ olefin}) / n(C_n \text{ olefin})$$

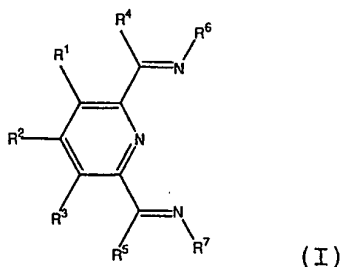
wherein  $n(C_n \text{ olefin})$  is the number of moles of olefin containing n carbon atoms, and  $n(C_{n+2} \text{ olefin})$  is the number of moles of olefin containing n+2 carbon atoms, or in other words the next higher oligomer of  $C_n$  olefin. From this can be determined the weight (mass) fractions of the various olefins in the resulting oligomeric reaction product mixture. The K factor is preferred to be in the range of about 0.65 to about 0.8 to make the  $\alpha$ -olefins of the most commercial interest. This factor can be varied to some extent, see for instance previously incorporated US6103946 and United States Appln. Ser. No. 09/906,974 (filed July 17, 2001), entitled "MANUFACTURING PROCESS FOR ALPHA-OLEFINS" (corresponding to PCT Appln. PCT/US01/22628, filed July 18, 2001).

CLAIMS

What is claimed is:

1. A method for reducing the formation of polyethylene waxes and polymers in a continuous process for the production of a linear  $\alpha$ -olefin product, said continuous process comprising the step of contacting, in a continuous reactor, process ingredients comprising an ethylene oligomerization catalyst composition, ethylene and a cocatalyst, wherein:

(a) the ethylene oligomerization catalyst composition comprises an iron complex of a compound of the formula



wherein:

$R^1$ ,  $R^2$  and  $R^3$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of  $R^1$ ,  $R^2$  and  $R^3$  vicinal to one another taken together may form a ring;

$R^4$  and  $R^5$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

$R^6$  and  $R^7$  are each independently a substituted aryl having a first ring atom bound to the imino nitrogen, provided that:

in  $R^6$ , a second ring atom adjacent to said first ring atom is bound to a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and further provided that

in  $R^6$ , when said second ring atom is bound to a halogen or a primary carbon group, none, one or two of the other ring atoms in  $R^6$  and  $R^7$  adjacent to said first ring atom are bound to a halogen or a primary carbon group, with the re-

mainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a secondary carbon group, none, one or two of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a halogen, a primary carbon group or a secondary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a tertiary carbon group, none or one of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a tertiary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; and

(b) the cocatalyst comprises an alkyl aluminum compound;

said method for reducing comprising the step of contacting said process ingredients in amounts such that the molar ratio of Al in the cocatalyst to Fe in the ethylene oligomerization catalyst is about 2000 or less.

2. The method of claim 1, wherein said molar ratio is from about 100 to about 1500.

3. The method of claim 1, wherein said molar ratio is from about 300 to about 1000.

4. The method of claim 1, wherein said molar ratio is from about 500 to about 700.

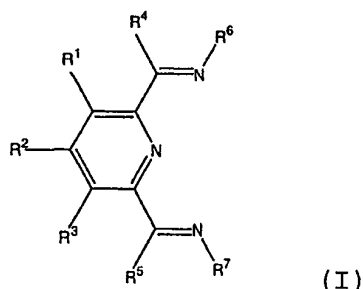
5. The method of claim 1, wherein said molar ratio is from about 5 to about 300.

6. The method of claim 1, wherein the continuous reactor is essentially single phase liquid full.

7. A continuous process for the production of a linear  $\alpha$ -olefin product, the process comprising the step of contacting, in a continuous reactor, process ingredients com-

prising an ethylene oligomerization catalyst composition, ethylene and a cocatalyst, wherein:

(a) the ethylene oligomerization catalyst composition comprises an iron complex of a compound of the formula



wherein:

$R^1$ ,  $R^2$  and  $R^3$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group, provided that any two of  $R^1$ ,  $R^2$  and  $R^3$  vicinal to one another taken together may form a ring;

$R^4$  and  $R^5$  are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

$R^6$  and  $R^7$  are each independently a substituted aryl having a first ring atom bound to the imino nitrogen, provided that:

in  $R^6$ , a second ring atom adjacent to said first ring atom is bound to a halogen, a primary carbon group, a secondary carbon group or a tertiary carbon group; and further provided that

in  $R^6$ , when said second ring atom is bound to a halogen or a primary carbon group, none, one or two of the other ring atoms in  $R^6$  and  $R^7$  adjacent to said first ring atom are bound to a halogen or a primary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in  $R^6$ , when said second ring atom is bound to a secondary carbon group, none, one or two of the other ring atoms in  $R^6$  and  $R^7$  adjacent to said first ring atom are bound to a

halogen, a primary carbon group or a secondary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; or

in R<sup>6</sup>, when said second ring atom is bound to a tertiary carbon group, none or one of the other ring atoms in R<sup>6</sup> and R<sup>7</sup> adjacent to said first ring atom are bound to a tertiary carbon group, with the remainder of the ring atoms adjacent to said first ring atom being bound to a hydrogen atom; and

(b) the cocatalyst comprises an alkyl aluminum compound;

characterized in that the molar ratio of Al in the cocatalyst to Fe in the ethylene oligomerization catalyst is from about 5 to about 300.

8. The process of claim 7, wherein the continuous reactor is essentially single phase liquid full.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/24297

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C2/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 27124 A (E.I. DU PONT DE NEMOURS) 25 June 1998 (1998-06-25) claims	1
A	US 5 955 555 A (BENNETT ALISON MARGARET ANNE) 21 September 1999 (1999-09-21) cited in the application claims	1
A	WO 00 15646 A (BP CHEMICALS) 23 March 2000 (2000-03-23) claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

15 November 2001

Date of mailing of the international search report

23/11/2001

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Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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Authorized officer

Van Geyt, J

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/24297

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			BR 9714219 A	18-04-2000
			EP 1127897 A2	29-08-2001
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			WO 0015646 A1	23-03-2000





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C07F 13/00, 15/00, 15/02, 15/04 // C08F 10/00</b>		A1	(11) International Publication Number: <b>WO 00/08034</b>
			(43) International Publication Date: 17 February 2000 (17.02.00)
(21) International Application Number: PCT/GB99/02498 (22) International Filing Date: 30 July 1999 (30.07.99) (30) Priority Data: 9817004.6 6 August 1998 (06.08.98) GB (71) Applicant (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): GIBSON, Vernon, Charles [GB/GB]; Flat 2, 46 Prince's Gate, Exhibition Road, London SW7 2QA (GB). McTAVISH, Stuart, James [GB/GB]; Maisonette Flat, 475 Fulham Road, London SW6 1HL (GB). (74) Agent: SMITH, Julian, Philip, Howard; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.	
(54) Title: PREPARATION OF POLYMERISATION CATALYSTS			
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>(B)</p> </div> <div style="text-align: center;"> <p>Ligand (B)</p> </div> </div>			
(57) Abstract			
<p>A process is described for producing a transition metal complex of formula (B) wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand (B) and (2) a compound of the formula M[T]-(T/b)X. The complex has utility as a catalyst for the polymerisation of 1-olefins.</p>			

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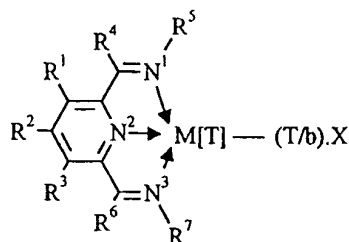
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### PREPARATION OF POLYMERISATION CATALYSTS

The present invention relates to a novel process for preparing transition metal compounds used as polymerisation catalysts.

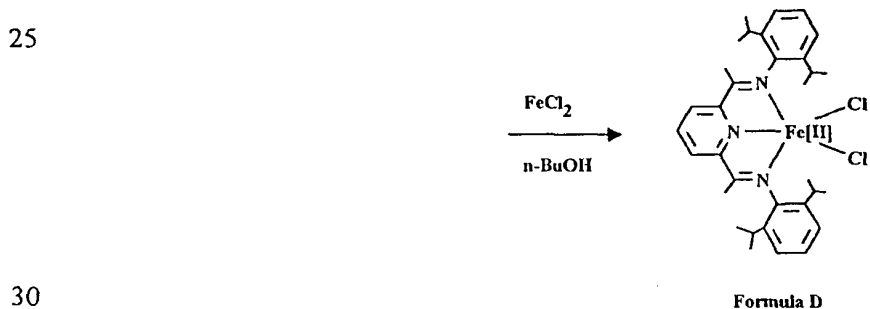
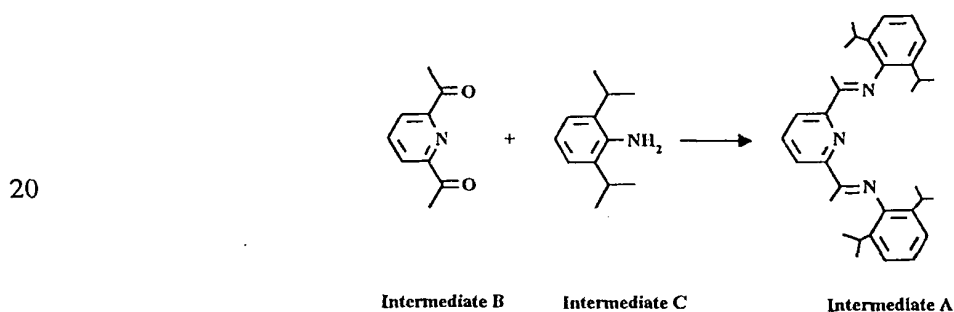
The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. In recent years the use of certain metallocene catalysts (for example biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity and capable of providing an improved distribution of the comonomer units. Most recently, WO98/27124 has disclosed that ethylene may be polymerised by contacting it with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacetylpyridinebis(imines); and our own copending application WO 99/12981 has disclosed novel nitrogen-containing transition metal compounds comprising the skeletal unit depicted in Formula B:



Formula B

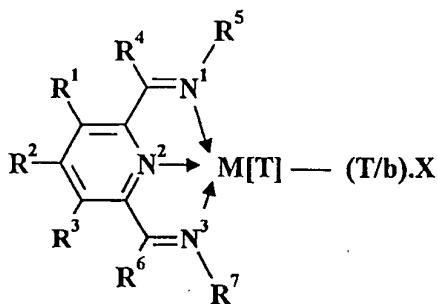
wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the  
 5 valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

10 The above transition metal complexes are disclosed as being made by first forming the ligand (eg Examples 1 to 6 of WO 98/27124) and then separately reacting the ligand with the desired metal salt such as FeCl<sub>2</sub> or CoCl<sub>2</sub> (eg Examples 7 to 17 of WO 98/27124) to form the complex. This route is also exemplified in WO 99/12981, for example in the synthesis of 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub> (Formula D  
 15 below), where the reaction scheme is shown as follows:



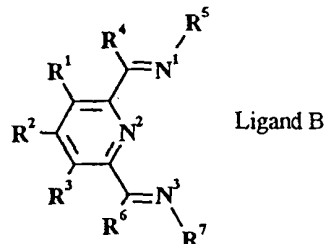
Hitherto, it has been considered necessary to complete the reaction between Intermediates B and C to form Intermediate A (the ligand), and to isolate Intermediate A from Intermediates B and C prior to reacting with the transition metal compound to form the transition metal complex compound (Formula B). However we have now discovered that this two step process can in fact be performed as a single stage reaction, using, for example, a single reaction vessel. This provides substantial process and economic advantages.

Accordingly a first aspect of the present invention provides a process for producing a transition metal complex of the formula



Formula B

wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand B

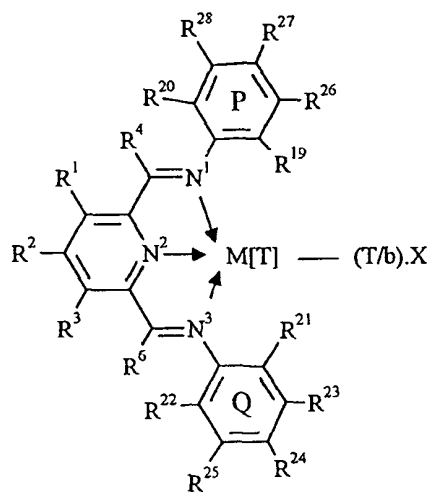


and (2) a compound of the formula  $M[T]-(T/b)X$ .

The reaction is preferably carried out in a single reaction vessel.

In the process of the present invention, the final product is obtained directly in a single stage reaction, without the need for any additional process steps: however at a molecular level the reaction may of course still proceed through more than one step.

Preferred transition metal complexes to be made by the process of the present invention comprise the skeletal unit depicted in Formula Z:



Formula Z

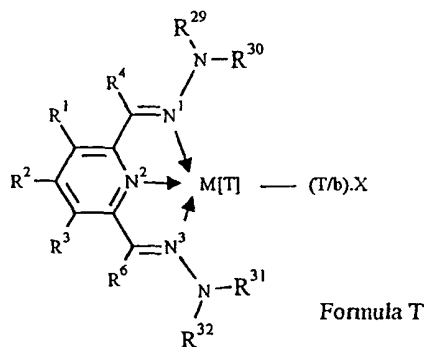
wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the

- valency of the atom or group X;  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted
- 5 heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; with the proviso that at least one of  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl when neither of the ring systems P and Q forms part of a polyaromatic fused-ring system. In this particular aspect of the present invention, in the case that neither of the ring systems
- 10 P and Q forms part of a polyaromatic ring system, it is preferred that at least one of  $R^{19}$  and  $R^{20}$ , and at least one of  $R^{21}$  and  $R^{22}$  is selected from hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, and most preferably each of  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  is selected from hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. The atom or group represented by
- 15 X is preferably halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.
- 20 Subject to the foregoing provisos regarding  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  in Formula Z,  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  in the compounds depicted in Formulae B and Z of the present invention are preferably independently selected from hydrogen and  $C_1$  to  $C_8$  hydrocarbyl, for example, methyl, ethyl, n-propyl, n-butyl, n-hexyl, and n-octyl. In Formula B,  $R^5$  and  $R^7$  are preferably independently selected from substituted or
- 25 unsubstituted alicyclic, heterocyclic or aromatic groups, for example, phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5 dichloro-2,6-diethylphenyl, and
- 30 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl and pyridinyl.

The ring systems P and Q in Formula Z are preferably independently 2,6-hydrocarbylphenyl or fused-ring polyaromatic, for example, 1-naphthyl, 2-naphthyl, 1-

phenanthrenyl and 8-quinoliny.

A further aspect of the present invention provides process for producing a transition metal complex having the Formula T:



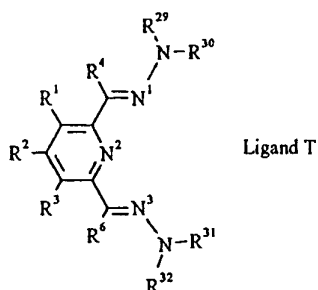
wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV],

20 Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X;  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{29}$  to  $R^{32}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{29}$  to  $R^{32}$  are

25 hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents,

comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand T





and (2) a compound of the formula  $M[T]-(T/b)X$ .

10        Examples of complexes which may be made by the process of the invention include 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridine(2,6-diisopropylanil)CoCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,6-dimethylanil)FeCl<sub>2</sub>, and 2,6-diacetylpyridinebis(2,4-dimethylanil)FeCl<sub>2</sub>.

15

In the process of the present invention it is preferred that the components (1) and (2) of the reaction are brought together substantially simultaneously. However, if desired, they may be brought together in quick succession in any order.

Preferably the reaction between components (1) and (2) is carried out in the presence of an acidic catalyst. Examples of acidic catalysts include glacial acetic acid, p-toluenesulphonic acid and formic acid.

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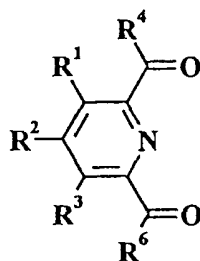
It is preferred to carry out the reaction in the presence of a liquid diluent. Most preferably the diluent is a solvent for one or more of the components of the reaction. Examples of suitable liquid diluents are liquid hydrocarbons, for example toluene, xylene, hexane and cyclohexane, or alcohols, for example, ethanol, isopropanol or 1-butanol.

25

The reaction is preferably carried out at temperatures between 0°C and 150°C. Preferably the reaction is heated, typically to a temperature between 50°C and 130°C, more usually to between 70 to 110°C.

30        The time for the reaction may be, for example, from 5 minutes to 72 hours, though it is more usually between 12 and 48 hours, typically 18 to 36 hours.

The ligand precursors employed in the reaction process of the present invention to make the "Ligand B" preferably comprise a compound of the Formula K

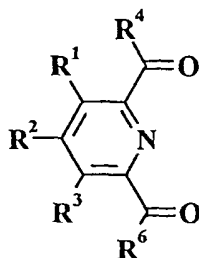


Formula K

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plus compounds  $H_2NR^5$  and  $H_2NR^7$ , where  $R^1$  to  $R^7$  are as defined above. When  $R^5$  and  $R^7$  are the same, two equivalents of the same amine compound are of course used. When  $R^5$  and  $R^7$  are the different and two amines are used, a mixture of products may be obtained, with  $R^5$  and  $R^7$  being either the same or different on an individual molecule. The ligand precursors employed in the reaction to make the "Ligand T" preferably comprise a compound of the Formula K

20



Formula K

25

plus compounds  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$ , where  $R^1$  to  $R^4$ ,  $R^6$ ,  $R^{29}$ ,  $R^{30}$ ,  $R^{31}$  and  $R^{32}$  are as defined above. When  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$  are the same, two equivalents of the same amine compound are used. When  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$  are the different, a mixture of products may be obtained, with  $-NR^{29}R^{30}$  and  $-NR^{31}R^{32}$  being either the same or different on an individual molecule.

30

In the process of the present invention, M and X in the compound of the formula  $M[T]-(T/b)X$  [component (2)] are as defined in the Formulae B, Z and T as set out above. Examples of compounds of the formula  $M[T]-(T/b)X$  are  $FeCl_2$ ,  $MnCl_2$ ,  $CoCl_2$ ,  $FeBr_2$ ,  $CoBr_2$  and  $FeCl_3$ . Preferred metals M[T] are Fe[II], Fe[III], Co[II] and Co[III].

5 The process of the present invention can be used to produce mixtures of complexes containing two or more different transition metals, for example, by employing two or more different transition metal compounds of formula  $M[T]-(T/b)X$  as the component (2).

The complexes made according to the process of the invention may be used  
10 directly as polymerisation catalysts. Alternatively they may be combined with an activator. The activator compound is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable organoaluminium compounds include trialkylaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride,  
15 diethylaluminium chloride and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic  
20 alumoxanes can be represented by the formula  $[R^{16}AlO]_s$  and the linear alumoxanes by the formula  $R^{17}(R^{18}AlO)_s$  wherein s is a number from about 2 to 50, and wherein  $R^{16}$ ,  $R^{17}$ , and  $R^{18}$  represent hydrocarbyl groups, preferably  $C_1$  to  $C_6$  alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable hydrocarbylboron compounds are  
25 dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate,  $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$ , trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

30 The quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron compounds for the process for making the polymerisation catalyst is easily determined by simple testing, for example, by the preparation of small test

samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per Fe, Co, Mn or Ru metal atom in the compound of Formula B.

5           If desired, the preparation of the polymerisation catalyst can be carried out in the same vessel as the preparation of the transition metal complex by the process of the present invention.

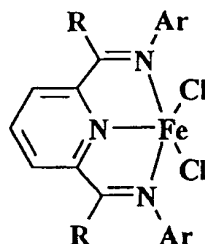
Catalysts made with complexes prepared according to the present invention can be unsupported or supported on a support material, for example, silica, alumina, or  
10    zirconia, or on a polymer or prepolymer, for example polyethylene, polystyrene, or poly(aminostyrene). If desired the catalysts can be formed *in situ* in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts can if desired be supported on a heterogeneous catalyst, for example, a  
15    magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal compounds of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating  
20    the volatile diluent. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

If it is desired to use the catalyst on a support material (see below), this can be achieved, for example, by preforming the catalyst system comprising the transition metal  
25    complex and the activator and impregnating the support material preferably with a solution thereof, or by introducing to the support material one or more of the components simultaneously or sequentially.

### EXAMPLES

#### 30    Preparation of complexes

2,6-pyridyldiimine iron(II)dichloride complexes of the formula below were produced by the process of the invention.



- 1 R=H, Ar = 2,4,6-trimethylanil  
 2 R = Me, Ar = 2,4,6-trimethylanil  
 3 R = H, Ar = 2,6-diethylanil

### Example 1

#### Preparation of 1 - [2,6-dialdiminepyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

To a schlenk tube, under a nitrogen atmosphere, 2,6-pyridinedicarboxaldehyde (1.2eqs, 0.054g, 0.397mmol), anhydrous iron(II)dichloride (1eq, 0.042g, 0.331mmol) and 2,4,6-trimethylaniline (2.5eq, 0.12ml, 0.828 mmol) were added followed by *n*-butanol (40ml, dry) to form a yellow suspension. The reaction mixture was heated at 80°C for 20h to produce a brown precipitate. Solvent removed at the pump and the residue washed, ether (6x30ml) to yield a brown solid (0.101g, 62%),

1. FAB<sup>+</sup> MS *m/z* 495 [M<sup>+</sup>], 460 [M<sup>+</sup>-Cl], 422 [M<sup>+</sup>-2Cl], 368 [M<sup>+</sup>-FeCl<sub>2</sub>].

IR  $\nu(\text{C}=\text{N})$  1632cm<sup>-1</sup>. No other C=N peaks were observed in the IR.

### Example 2

#### Preparation of 2 - [2,6-diacetylpyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

To a schlenk tube, under a nitrogen atmosphere, 2,6-diacetylpyridine (1.2eq, 0.054g, 0.397mmol), anhydrous iron(II)dichloride (1eq, 0.042g, 0.331mmol), 2,4,6-trimethylaniline (2.5eq, 0.12ml, 0.828 mmol) and glacial acetic acid (3 drops, catalyst) were added followed by *n*-butanol (40ml, dry). The reaction mixture was heated at 80°C for 24h to produce a dark blue precipitate. Solvent removed at the pump and the residue washed, ether (4x30ml) to yield a dark blue solid (0.137g, 83%),

2. FAB<sup>+</sup> MS *m/z* 523 [M<sup>+</sup>], 488 [M<sup>+</sup>-Cl], 453 [M<sup>+</sup>-2Cl]

Example 3Preparation of 3- [2,6-diacetylpyridinebis(2,6-diethylanil) FeCl<sub>2</sub>]

Anhydrous iron(II)dichloride (0.095g, 0.750mmol) 2,6-pyridinedicarboxaldehyde (1.2eq, 0.122g, 0.900mmol), and 2,6-diethylaniline (2.5eq, 0.310ml, 1.875 mmol) were added to a Schlenk tube, followed by n-butanol (40ml), and were heated at 80°C for 48h. A green precipitate appeared after 10min. Solvent was removed at the pump to yield, upon washing with ether (4 x 40ml), a green solid. FAB<sup>+</sup> MS *m/z* 523 [M<sup>+</sup>], 488 [M<sup>+</sup>-Cl], 453 [M<sup>+</sup>-2Cl].

10

Polymerisation using complexes prepared above

To a Schlenk tube, catalyst (0.01mmol) and toluene (40ml, dry) were added followed by methylalumoxane (10%w/w in toluene, 100eq, 0.65ml, 1.00mmol) to form an orange solution. The Schlenk tube was placed in a water bath at ambient temperature. Ethylene atmosphere (1 bar) was passed over the solution for 30 minutes. The reaction was then quenched by addition of dilute HCl (40ml), and the resulting polymer filtered and washed with methanol (3x50ml) to yield, upon drying in vacuum oven, solid polyethylene.

20 Example 4Polymerisation using 1 - [2,6-dialdiminepyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

Complex 1, (0.01mmol, 4.96mg), yielded 6.20g polyethylene giving an activity of 1240 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup>.

PE, M<sub>w</sub>= 46000, PDI= 18.0, M<sub>PK</sub>= 1400

25

Example 5Polymerisation using 2 - [2,6-diacetylpyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

Complex 2, (0.01mmol, 5.24mg), yielded 4.35g polyethylene giving an activity of 870 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup>.

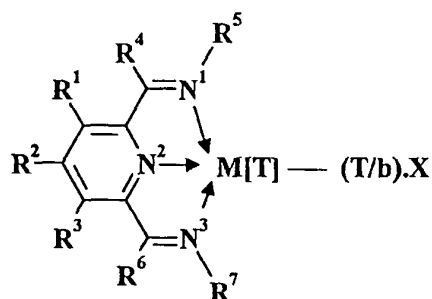
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PE, M<sub>w</sub>= 80 000, PDI= 21.0, M<sub>PK</sub>= 70 000.

These results show that the process of the invention provides catalysts which are as effective as those produced by the known two-stage process.

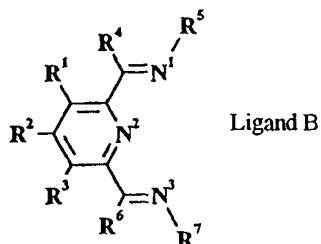
## Claims:

1. Process for producing a transition metal complex of the formula



10

- wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the
- 15 wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents;
- 20 comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand B

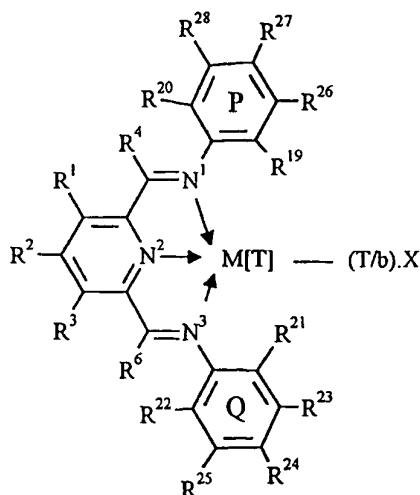


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and (2) a compound of the formula  $M[T]-(T/b)X$ .

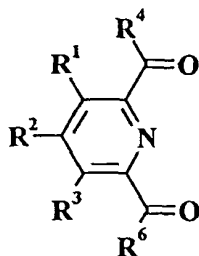
2. Process according to claim 1 which is carried out in a single reaction vessel.
- 10 3. Process according to claim 1 or 2 wherein components (1) and (2) of the reaction are brought together substantially simultaneously.
4. Process according to any preceding claim wherein the reaction between components (1) and (2) is carried out in the presence of an acidic catalyst.
5. Process according to claim 4 wherein the acidic catalyst comprises glacial acetic
- 15 acid, p-toluenesulphonic acid or formic acid.
6. Process according to any preceding claim wherein the reaction is carried out in the presence of a liquid diluent.
7. Process according to claim 6 wherein the diluent comprises toluene, xylene, hexane, cyclohexane, ethanol, isopropanol or 1-butanol.
- 20 8. Process according to any preceding claim wherein the reaction is carried out at a temperature of from 50°C to 130°C.
9. Process according to any preceding claim wherein the transition metal complex has the skeletal unit depicted in Formula Z:





Formula Z

- 15 wherein  $M$  is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV];  $X$  represents an atom or group covalently or ionically bonded to the transition metal  $M$ ;  $T$  is the oxidation state of the transition metal  $M$  and  $b$  is the valency of the atom or group  $X$ ;  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; with the proviso that at least one of  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl when
- 25 neither of the ring systems  $P$  and  $Q$  forms part of a polyaromatic fused-ring system.
10. Process according to claim 9 wherein the reactants comprise
- (1a) a compound of the Formula K

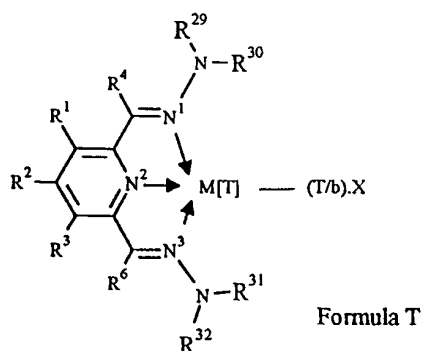


Formula K

- 5
- 10 (1b) compounds having the formulae  $H_2NR^5$  and  $H_2NR^7$ , and  
 (2) a compound of the formula  $M[T]-(T/b)X$ .
11. Process according to any preceding claim wherein  $R^5$  and  $R^7$  are independently  
 selected from phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl,  
 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-  
 15 butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-  
 butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-  
 bromo-2,6-dimethylphenyl, 3,5 dichloro-2,6-diethylphenyl, and 2,6-bis(2,6-  
 dimethylphenyl)phenyl, cyclohexyl and pyridinyl.
12. Process according to any of claims 1 to 8 wherein the transition metal complex  
 20 has the skeletal unit depicted in Formula T:

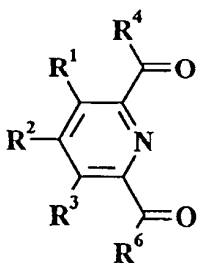
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- 10 wherein  $R^{29}$  to  $R^{32}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more thereof are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.
- 15 13. Process according to claim 12 wherein the reactants comprise (1a) a compound of the Formula K

20



Formula K

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- (1b) compounds having the formulae  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$ , and  
 (2) a compound of the formula  $M[T]-(T/b).X$ .

14. Process according to any preceding claim wherein X comprises halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxide, carboxylate,  
 30 hydrocarbyl, substituted hydrocarbyl or heterohydrocarbyl.

15. Process according to claim 14 wherein X comprises chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.
16. Process according to any preceding claim wherein M[T] comprises Fe[II],  
5 Fe[III], Co[II] or Co[III].
17. Process according to any of claims 1 to 11, wherein the transition metal complex comprises 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridine(2,6-diisopropylanil)CoCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-  
10 diacetylpyridinebis(2,6-dimethylanil)FeCl<sub>2</sub>, or 2,6-diacetylpyridinebis(2,4-dimethylanil)FeCl<sub>2</sub>.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02498

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F13/00 C07F15/00 C07F15/02 C07F15/04 //C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BLACK, DAVID ST. CLAIR ET AL: "Template synthesis of metal complexes containing new macrocyclic ligand systems" TETRAHEDRON LETT. (1978), (31), 2835-6, 1978, XP002117950 the whole document	1
A	WO 98 27124 A (E.I. DU PONT DENOURS AND COMPANY) 25 June 1998 (1998-06-25) cited in the application examples	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

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Information on patent family members

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